Technical Report

Evaluation of Resistively Heated Metal Monolith Catalytic Converters On An M100 Neat Methanol-Fueled Vehicle

Part II

by

Gregory K. Piotrowski

December 1989

NOTICE

Technical Reports do not necessarily represent final EPA decisions or positions. They are intended to present technical analysis of issues using data which are currently available. The purpose in the release of such reports is to facilitate the exchange of technical information and to inform the public of technical developments which may form the basis for a final EPA decision, position or regulatory action.

U. S. Environmental Protection Agency
Office of Air and Radiation
Office of Mobile Sources
Emission Control Technology Division
Control Technology and Applications Branch
2565 Plymouth Road
Ann Arbor, Michigan 48105



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY ANN ARBOR. MICHIGAN 48105

JAN 18

OFFICE OF AIR AND RADIATION

MEMORANDUM

SUBJECT: E	Exemption	From	Peer	and	Administrative	Review
------------	-----------	------	------	-----	----------------	--------

FROM:

Karl H. Hellman, Chief

Control Technology and Applications Branch

TO:

Charles L. Gray, Jr., Director

Emission Control Technology Division

The attached report entitled "Evaluation of Resistively Heated Metal Monolith Catalytic Converters On An M100 Neat Methanol-Fueled Vehicle - Part II" (EPA/AA/CTAB/89-09), describes the evaluation of palladium/cerium and base metal catalysts on resistively heated metal monolith substrates. The test vehicle was an M100-fueled 1981 Volkswagen Rabbit.

Since this report is concerned only with the presentation of data and its analysis and does not involve matters of policy or regulations, your concurrence is requested to waive administrative review according to the policy outlined in your directive of April 22, 1982.

Conc	urrence:_		le May			16-20
	C	harles L.	Gray, Jt.	Dir., EC	CTD	

cc: E. Burger, ECTD

Table of Contents

			rage umber
I.	Summary		1
II.	Introduction		2
III.	Catalytic Converter Description		3
IV.	Vehicle Description	•	4
v.	Test Facilities and Analytical Methods	•	4
VI.	Test Procedure		5
VII.	Discussion of Test Results		5
VIII.	.Highlights From Testing		20
IX.	Acknowledgments	•	20
x.	References		21

I. Summary

Two catalyst formulations using resistively heated metal monolith substrates were evaluated for the application of exhaust emission catalysts on an M100 neat methanol-fueled vehicle. The active catalyst formulations were palladium:cerium (Pd:Ce) and a base metal formulation. The catalysts were evaluated at low mileage in two modes:

- 1. Resistive heating applied to the substrate during initial portions of the cold-start and hot-start transient segments of the test cycle (the Federal test procedure (FTP)); [1] and
- 2. No resistive heating applied to the substrate during the driving cycle.

The test vehicle was also driven in the baseline, or no-catalyst mode, to obtain engine-out emission levels for comparison.

Resistively heating the Pd:Ce catalyst provided a substantial emissions control benefit over the non-resistively heated catalyst mode, for emissions measured as hydrocarbons (HC), methanol (CH₃OH), and formaldehyde (HCHO). Efficiencies from baseline levels for these pollutants with the resistively heated Pd:Ce converter over the FTP were 94, 92, and 99 percent, respectively. The HCHO levels measured, 2.0 milligrams/mile over the FTP, were low compared with other catalysts previously evaluated at low mileage by EPA.

The base metal catalyst showed a slight improvement in emissions of HC, CH₃OH, and HCHO when the catalyst was resistively heated. Generally, the base metal catalyst was not as efficient as the Pd:Ce catalyst in either the resistively heated or non-resistively heated modes.

The catalysts and resistively heated metal monolith substrates evaluated were provided by Camet, Inc., a subsidiary of W. R. Grace. The M100-fueled test vehicle was provided by Volkswagen of America.

II. Introduction

The major portion of emissions measured as hydrocarbons (HC) and formaldehyde (HCHO) emissions from a catalyst-equipped methanol-fueled vehicle over the FTP cycle are generated during cold start and warm-up of the catalyst.[2] These emissions are difficult to control because engine-out emissions are high and catalytic converters have low conversion efficiency during their warm-up phase of operation.

Heating parts of the engine or the catalytic converter at cold start may provide an emissions reduction benefit over the FTP cycle.[3] However, even if parts of the engine were hot enough to allow an engine's cold-start emissions to be as low as its hot-start emissions, Bag 1 emissions would still be higher because the catalyst would not light-off (come to operating temperature) until some time after cold start. Heating a large mass of engine metal at cold start may be costly from an economic standpoint also. Resistively heating a catalytic converter at cold start may be a feasible concept if the electrical power requirement for heating is not excessive and resistive heating is required for only a limited period of time while the vehicle is operated.

Resistively heated metal monolith catalytic converters have been previously evaluated by EPA.[3,4,5,6] testing of this technology [4] on a methanol-fueled vehicle utilized a platinum/palladium/rhodium mixture similar conventional three-way automotive catalysts. FTP Bag 1 levels of emissions measured as hydrocarbons and formaldehyde were 0.50 and 0.054 grams respectively when the catalytic converter was resistively heated for 30 seconds at cold start. These were improvements of 71 and 67 percent respectively over HC and HCHO levels from the same catalyst in the absence of resistive The lower Bag 1 emissions translated into weighted heating. average FTP levels of 0.05 grams per mile for emissions measured as HC and 5 milligrams per mile for HCHO.

One way to improve upon this technology would be changing the active catalyst mix to provide greater efficiency at the same economic cost or the same efficiency at lower cost. Palladium (Pd) is of great interest as a gasoline vehicle catalyst because of its lower cost with respect to platinum (Pt) and rhodium (Rh) as well as its increased availability due to its wide distribution throughout the earth's crust.[7,8] is less resistant to poisoning from fuel contaminants such as lead, phosphorus, and sulfur;[7] as neat methanol contains no additives, catalyst deactivation through poisoning is unlikely. Pd, then, may be a useful alternative to conventional three-way catalyst for a vehicle fueled with M100.

Base metal catalysts are also attractive for a methanol vehicle application because of their low cost and the absence of poisons like those mentioned above in the exhaust.[9] Base metal catalysts have been evaluated by the Control Technology and Applications Branch as methanol vehicle catalysts.[10] An efficient base metal catalyst utilizing the resistively heated substrate technology might provide a lower cost alternative to a conventional noble metal catalyst for the methanol vehicle application.

The manufacturers of the resistively heated substrate, Camet and W. R. Grace, agreed to supply EPA with substrates coated with two active catalysts not previously evaluated with this technology on a methanol-fueled vehicle:

- 1. A Pd, Cerium (Ce)-promoted configuration; and
- A base metal configuration.

The evaluation of these catalysts described in this report involved the use of the same methanol-fueled test vehicle mentioned in reference 4.

III. Catalytic Converter Description

The catalytic converters evaluated here were dual-bed configurations, consisting of an unheated metal monolith substrate and a smaller resistively heated metal monolith catalyst. This is the same substrate configuration that was evaluated on a methanol-fueled vehicle in reference 4.

The metal monoliths were resistively heated using a single 12-volt DC battery capable of providing 500-600 cold cranking amps. Voltage measured across the converter during heating was typically 9.5-9.9 volts. Current to the converter was typically measured at 350 and 250 amps at the start and after 1 minute of resistive heating, respectively. The period of resistive heating was limited to 10 seconds prior to and 50 seconds following cold start, and 5 seconds prior to and 30 seconds following hot start in the FTP cycle at 72°F soak conditions.

The dimensions of the converter are similar to those of typical underfloor catalysts on late model compact automobiles. The amperage draw was comparable to the maximum required by an automotive starter cranking in cold weather, although starter motors generally do not draw this high level of current for as long as the resistively heated catalyst does.

A description of the process for making the folded metal substrate may be found in a patent filed by Camet.[11] A detailed description of the substrate and its quick light-off characteristics have been published in an earlier report.[4]

The catalysts evaluated here were two separate compositions:

- Pd, with Ce promoter; and
- 2. A base metal composition.

The exact specifications of the catalyst compositions are considered proprietary to Camet and W. R. Grace.

IV. Vehicle Description

The test vehicle was a 1981 Volkswagen Rabbit 4-door sedan, equipped with automatic transmission, air conditioning, and radial tires. The 1.6-liter engine had a rated maximum power output of 88 horsepower at 5,600 rpm, when using neat methanol fuel. The vehicle was tested at 2,500 lbs inertia weight and 7.7 actual dynamometer horsepower. This vehicle was loaned to the U. S. EPA by Volkswagen of America.

A detailed description of the vehicle and special methanol modifications was provided in an earlier report.[4]

V. Test Facilities And Analytical Methods

Emissions testing at EPA was conducted on a Clayton Model ECE-50 double-roll chassis dynamometer, using a direct-drive variable inertia flywheel unit and road load power control unit. The Philco Ford constant volume sampler has a nominal capacity of 350 CFM. Exhaust HC emissions were measured with a Beckman Model 400 flame ionization detector (FID). CO was measured using a Bendix Model 8501-5CA infrared CO analyzer. NOx emissions were determined by a Beckman Model 951A chemiluminescent NOx analyzer.

Exhaust formaldehyde was measured using a dinitrophenyl-hydrazine (DNPH) technique.[12,13] Exhaust carbonyls including formaldehyde are reacted with DNPH solution forming hydrazine derivatives; these derivatives are separated from the DNPH solution by means of high performance liquid chromatography (HPLC), and quantization is accomplished by spectrophotometric analysis of the LC effluent stream.

The procedure developed for methanol sampling and presently in-use employs water-filled impingers through which are pumped a sample of the dilute exhaust or evaporative emissions. The methanol in the sample gas dissolves in water. After the sampling period is complete, the solution in the impingers is analyzed using gas chromatographic (GC) analysis.[14]

Most of the emission results in this report are computed using the methods outlined in the "Final Rule for Methanol Fueled Motor Vehicles and Motor Vehicle Engines," which was published in the Federal Register on Tuesday, April 11, 1989. Because these specialized procedures and calculation methods are not in widespread use, we have also included a hydrocarbon result which is what would be obtained if the exhaust was treated as if the fuel were gasoline. This is done as a convenience for the readers and users of the report who may be more familiar with hydrocarbon results obtained this way.

VI. Test_Procedure

This program had as its goal the reduction of unburned fuel and HCHO emissions from the test vehicle using two different active catalysts and a specific resistive heating strategy.

The test vehicle was emission tested in the baseline (no-catalyst) mode twice over the FTP cycle. catalyst was then placed in the exhaust stream and again tested twice over the FTP; no resistive heating was applied to the catalyst during this testing. The catalyst was resistively heated and emission tested six times over the FTP. The substrate was resistively heated for 10 seconds prior to cold start in Bag 1; the heating was continued for 50 seconds following cold start for a total heating time of 1 minute. The catalyst was also heated for 5 seconds prior to and 30 seconds following hot start in Bag 3, for a total time that heat was applied of 35 seconds. No resistive heating was applied during the Bag 2 portion of the test.

The Pd:Ce catalyst was then replaced with the base metal configuration provided by Camet. Two tests over the FTP were conducted without catalyst heating. The catalyst was then resistively heated using the scheme referred to above; three emission tests were conducted in this heated catalyst mode. The base metal catalyst was then removed from the exhaust and replaced with a straight pipe. Two additional baseline emission tests were conducted to conclude the data gathering phase of this report.

VII. Discussion of Test Results

Average Bag 1 (cold transient phase) emissions over the FTP for the various catalyst configurations tested are given in Table 1. Emission levels are described as grams per Bag 1 (grams/test phase) for all pollutants except HCHO; emissions of HCHO are reported as milligrams/Bag 1.

Table 1

Average Mass of Emissions

Bag 1 of FTP Cycle

Catalyst Configuration	HC*	CH ₄ (g)	HC**	OMHCE (g)	CH ₃ OH (g)	CO (g)	NOx (g)	HCHO (mg)
Baseline (no catalyst)	5.90	0.05	1.23	7.89	13.78	30.6	6.5	1159.0
Pd:Ce (no heat)	3.02	0.05	0.21	4.02	8.63	9.7	3.6	160.8
Pd:Ce (resistive heat)	0.86	0.06	0.10	1.19	2.94	9.1	3.3	29.5
Base metal (no heat)	3.08	0.04	0.31	4.12	8.56	16.2	6.5	242.2
Base metal (resistive heat)	2.38	0.06	0.33	3.14	6.32	14.6	6.4	167.8

Measured as hydrocarbons with a propane-calibrated FID.

^{**} Calculated per "Final Rule for Methanol Fueled Motor Vehicles and Motor Vehicle Engines."

The baseline (no catalyst) configuration used a straight pipe in the place of the underfloor converter. "No heat" refers to the evaluated catalyst tested without resistive heating applied to the substrate. Two hydrocarbon (HC) emission categories are listed in Table 1. The first category refers to emissions measured as HC with a FID calibrated with propane; a FID response factor for methanol is not used. The second HC figure is calculated per the requirements of the methanol vehicle emissions rulemaking.

Bag 1 HC emission test results are displayed graphically in Figure 1. HC emissions in Bag 1 with the propane calibrated FID were approximately 3 grams with both the Pd:Ce and base metal catalysts. While these emissions with both catalysts were substantially reduced when the substrates were resistively heated, a greater assist was provided to the Pd:Ce catalyst.

Emissions measured as HC were reduced to 0.86 grams/Bag 1, a reduction of 85 percent from baseline levels, with the resistively heated Pd:Ce catalyst. The base metal catalyst in the heated mode reduced HC to 2.38 grams/Bag 1, a reduction of 60 percent from baseline levels.

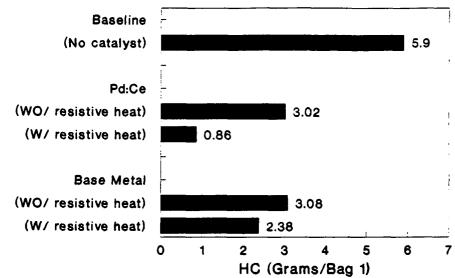
Methanol (CH₃OH) emission levels, displayed graphically in Figure 2, decreased substantially with resistive heating for both catalysts, yet the decrease with the Pd:Ce catalyst was greater. CH₃OH emissions were approximately 8.6 grams/Bag 1 with either catalyst in the non resistively heated mode. Heating the Pd:Ce catalyst caused CH₃OH emissions to drop to 2.94 grams/Bag 1, an efficiency of 79 percent from baseline levels. Average CH₃OH emissions decreased to 6.32 grams/Bag 1, a 54 percent efficiency from baseline levels, when the base metal converter was resistively heated.

CO emission levels over Bag 1 are given in Figure 3. Resistively heating each catalyst did not cause CO levels to be reduced below non-resistively heated catalyst levels with efficiencies as great as those experienced with HC and CH3OH CO was reduced to 9.7 grams/Bag with missions. non-resistively heated Pd:Ce configuration, an efficiency of 68 percent from baseline levels. Resistively heating the catalyst reduced CO further, to 9.1 grams/Bag 1, an incremental increase in efficiency of only 2 percent. The base metal catalyst reduced CO to 16.2 grams/Bag 1 without resistive heating for an efficiency from baseline of 47 percent. Resistively heating the catalyst lowered CO to 14.6 grams/Bag 1; this represents an incremental increase in efficiency of 5 percent from baseline levels.

Average Bag 1 NOx levels, depicted in Figure 4, decreased slightly with catalyst resistive heating for the Pd:Ce catalyst; the base metal catalyst did not appear effective for NOx conversion. From a baseline level of 6.5 grams/Bag 1, NOx

Figure 1
Bag 1 of CVS 75 (FTP) Cycle
Emissions Measured as HC*





*Measured as HC with a propane calibrated FID.

Figure 2
Bag 1 of CVS 75 (FTP) Cycle
Emissions of Methanol (CH3OH)

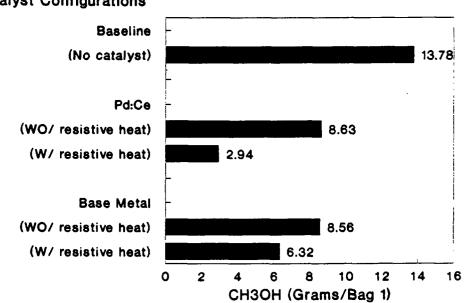


Figure 3
Bag 1 of CVS 75 (FTP) Cycle
CO Emissions



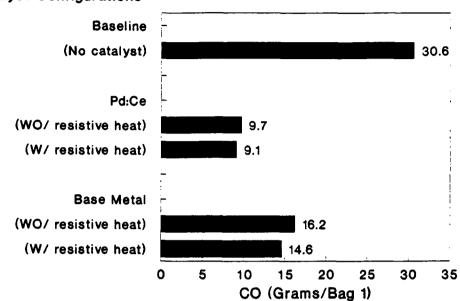
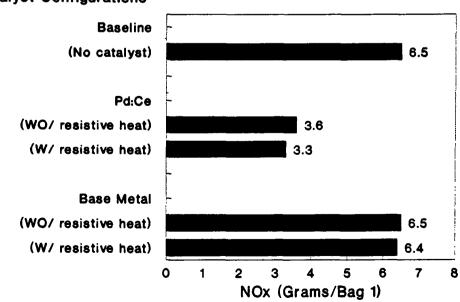


Figure 4
Bag 1 of CVS 75 (FTP) Cycle
NOx Emissions



was reduced to 3.3 grams/Bag 1 with the resistively heated Pd:Ce catalyst. The improvement attributed to resistive heating was only 0.3 grams/Bag 1 (non-resistively heated catalyst emissions less resistively heated catalyst emissions). The level of baseline emissions of NOx, 6.5 grams/Bag 1, did not change with the base metal converter, even when resistively heated; this catalyst appeared to be ineffective for NOx reduction in the manner in which it was evaluated here.

Bag 1 HCHO oxidation efficiency with either catalyst was greatly improved by resistive heating; HCHO levels over Bag 1 are given in Figure 5. The heated Pd:Ce catalyst had average Bag 1 HCHO emissions of 29.5 milligrams/Bag 1, an improvement of almost 82 percent from non resistively heated catalyst levels. HCHO efficiency was almost 98 percent from baseline with the heated Pd:Ce catalyst. Again, the base metal catalyst did not exhibit HCHO efficiencies as high as those from the Pd:Ce catalyst; the improvement caused by resistive heating was approximately 30 percent from non-resistively heated catalyst levels. HCHO emissions from the heated base metal catalyst were 167.8 milligrams/Bag 1, an efficiency of approximately 85 percent from baseline levels.

Table 2 contains emission averages over the Bag 3 (hot transient) portion of the FTP for the catalyst configurations evaluated. Resistive heating was applied for a period of 5 seconds preceding and 30 seconds following hot start for a total heating period of 35 seconds in Bag 3.

The Pd:Ce catalyst provided very high HC and CH₃OH efficiencies in Bag 3; a graphical summary of this data is given in Figures 6 and 7. In the unheated mode, emissions measured as HC and CH₃OH were reduced to 0.31 and 0.45 grams/Bag 1, respectively. These were efficiencies of 91 and 95 percent from baseline. Resistively heating this catalyst reduced these emission levels by half, to 0.16 and 0.19 grams/Bag 1, respectively. The base metal catalyst was not as effective in the unheated mode, and resistive heating did not improve the catalyst's performance to an efficiency equal to that of the noble metal catalyst. Bag 3 HC with the base metal catalyst was 1.08 grams, an efficiency from baseline of 68 percent; this level was essentially unchanged by resistive heating. Without resistive heating, the base metal catalyst reduced CH₃OH to 3.31 grams/Bag 3, an efficiency from baseline of 65 percent. Heating the base metal catalyst reduced CH₃OH further, to 2.66 grams/Bag 3, an efficiency of 72 percent.

Resistively heating either catalyst in Bag 3 appeared to reduce converter efficiency slightly for CO control. Figure 8 presents graphically CO levels obtained over Bag 3 for the

Table 2

Average Mass of Emissions

Bag 3 of FTP Cycle

Catalyst Configuration	HC* (q)	CH ₄	HC**	OMHCE (g)	CH ₃ OH	CO (g)	NOx (g)	HCHO
Baseline (no catalyst)	3.39	0.03	0.64	4.85	9.56	20.9	6.6	989.0
Pd:Ce (no heat)	0.31	0.02	0.16	0.38	0.45	0.7	2.7	60.0
Pd:Ce (resistive heat)	0.16	0.05	0.13	0.19	0.19	1.2	2.9	3.0
Base metal (no heat)	1.08	0.03	0.01	1.47	3.31	4.9	6.9	70.1
Base metal (resistive heat)	1.03	0.03	0.17	1.35	2.66	5.9	6.5	68.2

^{*} Measured as hydrocarbons with a propane-calibrated FID.

^{**} Calculated per "Final Rule for Methanol Fueled Motor Vehicles and Motor Vehicle Engines."

Figure 5
Bag 1 of CVS 75 (FTP) Cycle
Formaldehyde (HCHO) Emissions



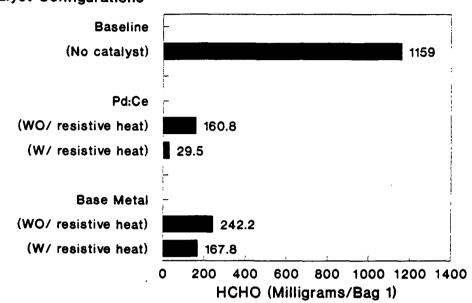
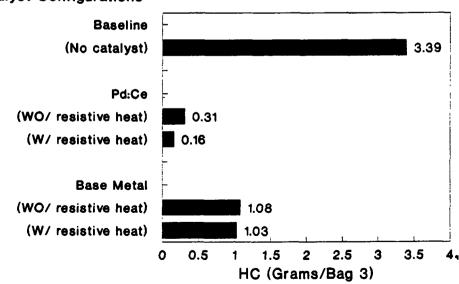


Figure 6
Bag 3 of CVS 75 (FTP) Cycle
Emissions Measured as HC*



*Measured as HC with a propane calibrated FID.

Figure 7
Bag 3 of CVS 75 (FTP) Cycle
Emissions of Methanol (CH3OH)

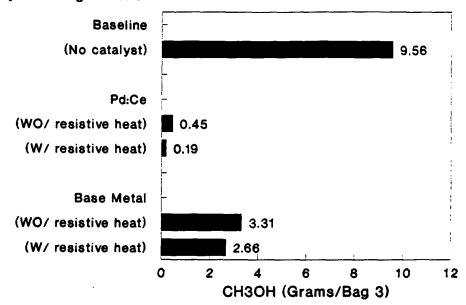
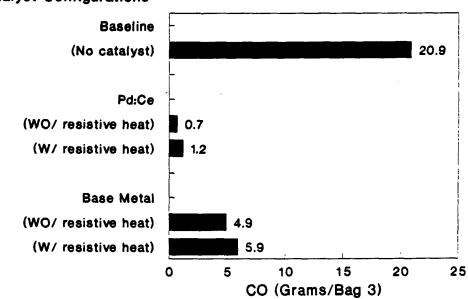


Figure 8
Bag 3 of CVS 75 (FTP) Cycle
CO Emissions



catalyst configurations tested. CO decreased to 0.7 grams/Bag 3 with the Pd:Ce catalyst, for an efficiency from baseline levels greater than 96 percent. CO increased slightly, to 1.2 grams/Bag 3, when resistive heating was applied to the Pd:Ce catalyst. The level of CO was also slightly increased when the base metal converter was heated. CO was measured at 5.9 grams/Bag 3 when resistive heating was applied, up from 4.9 grams/Bag 3 without resistive heating.

Recent testing of this resistively heated converter technology on a gasoline-fueled vehicle [6] at lower ambient temperatures suggested that reductions in CO following cold start were possible only with the addition of air in front of the converter. This excess air during catalyst resistive heating was supplied by an air pump in [6].

The testing reported on here involved a methanol, rather than a gasoline-fueled, vehicle. Also, the testing discussed in [6] was conducted at 20°F ambient, rather than 72°F ambient conditions. The gasoline-fueled vehicle may have been operating under significantly richer conditions during catalyst resistive heating than the methanol fueled test vehicle. Nevertheless, more work should be done to determine whether some excess air addition, even at 70°F conditions, is necessary to improve resistively heated catalyst CO efficiency with an M100 fueled engine.

Bag 3 NOx levels are given in Figure 9. Resistive heating did not noticeably improve the performance of the Pd:Ce catalyst for NOx control. Nox levels were essentially unchanged, approximately 2.8 grams over Bag 3, for both heated and unheated Pd:Ce configurations. The base metal converter, unheated or in the resistively heated mode, did not appear to be effective for NOx reduction.

Figure 10 displays HCHO levels over Bag 3 for the evaluated configurations. Bag 3 HCHO conversion efficiency of the Pd:Ce catalyst was greatly improved by resistive heating. HCHO emissions were reduced to 60 milligrams/bag with the unheated Pd:Ce converter; resistive heating lowered emissions from this configuration to 3 milligrams, an efficiency approaching virtually 100 percent from baseline levels. HCHO was reduced to 70 milligrams/Bag 3 for the base metal catalyst in the unheated mode, an efficiency of almost 93 percent from baseline levels. Resistively heating this catalyst, however, did not appreciably reduce Bag 3 HCHO below unheated catalyst levels.

Weighted average FTP emissions in units of mass/distance driven, for the various pollutant categories, are given in Table 3.

Figure 9
Bag 3 of CVS 75 (FTP) Cycle
NOx Emissions

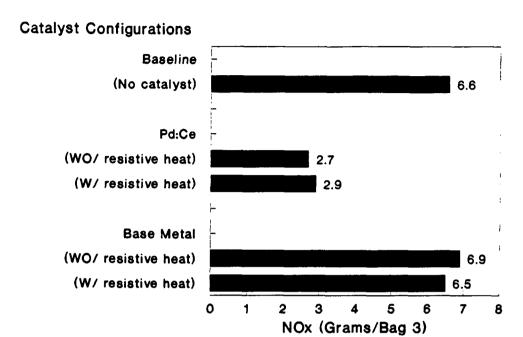
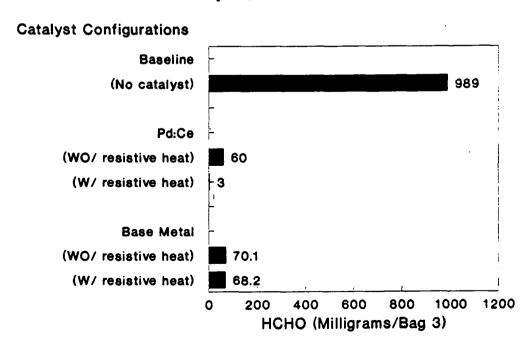


Figure 10
Bag 3 of CVS 75 (FTP) Cycle
Formaldehyde (HCHO) Emissions



Takle ?

Emissions Levels Over The FTP Cycle

Catalyst Configuration	HC* (g/mi)	CH₄ (g/mi)	HC** (g/mi)	OMHCE (g/mi)	CH ₃ OH (g/mi)	CO (g/mi)	NOx (g/mi)	HCHO (mg/mi)
Baseline (no catalyst)	1.07	0.01	0.20	1.48	2.65	6.6	1.4	293.0
Pd:Ce (no heat)	0.20	0.01	0.03	0.27	0.54	0.6	0.7	19.4
Pd:Ce (resistive heat)	0.06	0.01	0.02	0.08	0.20	0.6	0.7	2.0
Base metal (no heat)	0.29	0.01	0.03	0.37	0.76	1.6	1.5	22.0
Base metal (resistive (heat)	0.26	0.01	0.06	0.33	0.62	2.0	1.4	19.1

Measured as hydrocarbons with a propane-calibrated FID.

^{**} Calculated per "Final Rule for Methanol Fueled Motor Vehicles and Motor Vehicle Engines."

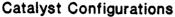
The improvements in HC efficiency caused by resistively heating the Pd:Ce catalyst in Bags 1 and 3 also substantially decreased weighted average HC emissions. Measured HC emissions were reduced to 0.06 grams/mile with the resistively heated Pd:Ce catalyst; this data is displayed in Figure 11. The base metal catalyst showed some improvement with resistive heating, but this improvement was minimal. Weighted FTP HC emissions were reduced to 0.26 grams/mile with the base metal catalyst resistively heated, an improvement of only 10 percent from the non-resistively heated configuration. Overall, the lowest measured HC level was obtained with the Pd:Ce catalyst in the resistively heated mode.

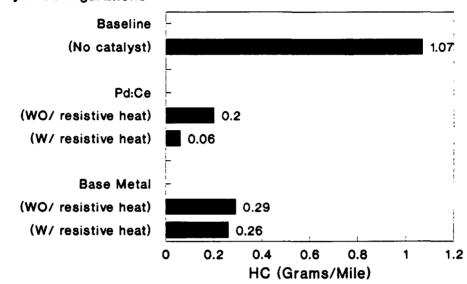
Figure 12 shows average CO levels over the FTP for the various configurations tested. Resistive heating did not increase CO efficiency for either catalyst in the manner in which each was tested here. Average CO over the FTP rose slightly, to 2.0 grams/mile, with the base metal catalyst resistively heated. Because both catalysts had slightly higher Bag 1 CO efficiencies, it may not be accurate to conclude that resistive heating contributed to increases in CO, however. It may be necessary to add air in front of the catalyst during the initial portion of Bag 1, even at 70°F ambient conditions, in order to substantially increase CO efficiency with resistive catalyst heating.[6]

NOx emissions over the FTP also did not substantially change when the catalysts were resistively heated; Figure 13 contains NOx emission averages over the FTP for all configurations tested. The Pd:Ce catalyst reduced average NOx emissions by half, while NOx was unaffected by the base metal catalyst. While the Pd:Ce catalyst reduced NOx emissions below 1.0 gram/mile, additional work would have to be done with this configuration to ensure attainment of 0.4 or 0.2 grams/mile levels.

Resistive heating greatly assisted the light-off of the noble metal catalyst for HCHO oxidation. Figure 14 shows FTP HCHO emission averages for the catalyst configurations tested. The Pd:Ce catalyst had substantial increases in HCHO efficiency in both Bags 1 and 3 with resistive heating, leading to a low weighted average of 2.0 milligrams/mile HCHO measured over the FTP. This level of HCHO from an M100-fueled vehicle is low with respect to many methanol vehicle catalysts which have been evaluated at low mileage by EPA.[3,4,7,8,13]

Figure 11
Weighted Average CVS 75 (FTP)
Emissions Measured as HC+





*Measured as HC with a propane calibrated FID.

Figure 12
Weighted Average CVS 75 (FTP)
CO Emissions

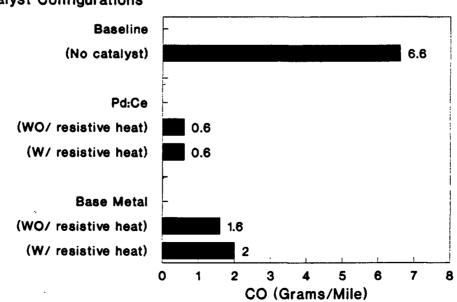


Figure 13
Weighted Average CVS 75 (FTP)
NOx Emissions



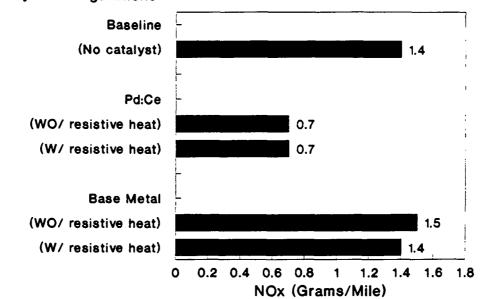
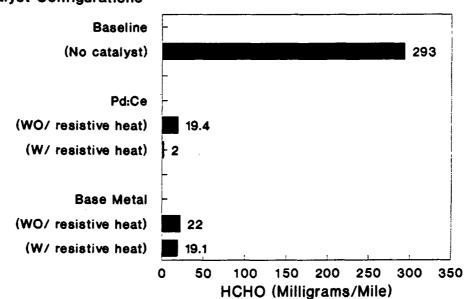


Figure 14
Weighted Average CVS 75 (FTP)
HCHO Emissions



VIII. Highlights From Testing

- 1. The resistively heated Pd:Ce converter had the highest emission control efficiencies of the configurations tested here.
- 2. Emissions measured as HC from a propane-calibrated FID were reduced to 0.06 grams/mile over the FTP with the resistively heated Pd:Ce converter. This was a 70 percent decrease in emissions from the level with the unheated Pd:Ce configuration; CH₃OH emissions were reduced by almost the same proportion. CH₃OH emissions were measured at an average of 0.20 grams/mile over the FTP with the resistively heated Pd:Ce catalyst.
- 3. HCHO emissions were reduced to a very low 2 milligrams/mile over the FTP with the resistively heated Pd:Ce catalyst. This decrease is primarily attributable to the 81 percent increase in efficiency in Bag 1 caused by resistive heating.
- 4. Average CO and NOx emissions over the FTP were not substantially affected by resistively heating either the Pd:Ce or base metal catalysts.
- 5. Emissions measured as HC and CH₃OH over the Bag 1 portion of the FTP were measured at similar levels with both the Pd:Ce and the base metal catalysts. Resistive heating was not as successful with the base metal catalyst; however, HC and CH₃OH were reduced an average 24 percent below nonresistively heated catalyst levels when the base metal catalyst was heated.
- 6. HCHO emissions were reduced to an average 19.1 milligrams/mile over the FTP with the resistively heated base metal catalyst. While this represents an efficiency of greater than 93 percent from baseline levels, the average HCHO level of 2.0 milligrams/mile with the heated Pd:Ce catalyst was much lower.

IX. Acknowledgments

The catalysts evaluated in this test program were supplied by Camet, located in Hiram, Ohio. Camet is a manufacturer and sales agent for W. R. Grace and Company. The methanol-fueled test vehicle was supplied by Volkswagen of America.

The author appreciates the efforts of Ernestine Bulifant, Robert Moss, and Rodney Branham of the Test and Evaluation Branch, ECTD, who conducted the driving cycle tests and prepared the methanol and formaldehyde samples for analysis. The author also appreciates the efforts of Jennifer Criss and Diane Descavish of CTAB, ECTD, for word processing and editing support.

X. References

- 1. 1975 Federal Test Procedure, <u>Code</u> of <u>Federal</u> <u>Regulations</u>, Title 40, Part 86, Appendix I(a), Urban Dynamometer Driving Schedule.
- 2. Improved Control of Formaldehyde by Warmup of Catalyst Prior to Vehicle Start, Memorandum, Piotrowski, G. K., OAR, OMS, ECTD, Ann Arbor, MI, 1985.
- 3. "Resistive Materials Applied To Quick Light-Off Catalysts," SAE Paper 890799, Hellman, K. H., et al., March 1989.
- 4. "Evaluation of a Resistively Heated Metal Monolith Catalytic Converter on an M100 Neat Methanol-Fueled Vehicle," Blair, D. M. and G. K. Piotrowski, EPA/AA/CTAB/88-08, August 1988.
- 5. "Evaluation of a Resistively Heated Metal Monolith Catalytic Converter on a Gasoline-Fueled Vehicle," Piotrowski, G. K., EPA/AA/CTAB/88-12, December 1988.
- 6. "A Resistively Heated Catalytic Converter With Air Injection For Oxidation of Carbon Monoxide and Hydrocarbons At Reduced Ambient Temperatures," Piotrowski, G. K., EPA/AA/CTAB/89-06, September 1989.
- 7. "Uses of Palladium in Automotive Emission Control Catalysts," SAE Paper 880281, Summers, J. C., et al., March 1988.
- 8. "Durability of Palladium Only Three-Way Automotive Emission Control Catalysts," SAE Paper 890794, Summers, J. C., et al., March 1989.
- 9. "Low Mileage Catalysts Evaluation with a Methanol-Fueled Rabbit Second Interim Report," Wagner, R. D. and L. C. Landman, EPA/AA/CTAB/TA/84-3, June 1984.
- 10. "Evaluation of Emissions from Low Mileage Catalysts on a Light-Duty Methanol-Fueled Vehicle," Piotrowski, G. K., EPA/AA/CTAB/87-05.
- 11. "Process For Making Metal Substrate Catalytic Converter Cores," Cornelison, R. C. and W. B. Retallick, U.S. Patent 4,711,009, December 8, 1987.
- 12. Formaldehyde Measurement In Vehicle Exhaust At MVEL, Memorandum, Gilkey, R. L., OAR, OMS, EOD, Ann Arbor, MI, 1981.

- 13. "Formaldehyde Sampling From Automobile Exhaust: A Hardware Approach," Pidgeon W., EPA/AA/TEB/88-01, July 1988.
- 14. "Sample Preparation Techniques For Evaluating Methanol and Formaldehyde Emissions From Methanol-Fueled Vehicles and Engines," Pidgeon, W. and M. Reed, EPA/AA/TEB/88-02, September 1988.